AD-785 634

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Joyce L. Illinger, et al

Army Materials and Mechanics Research Center
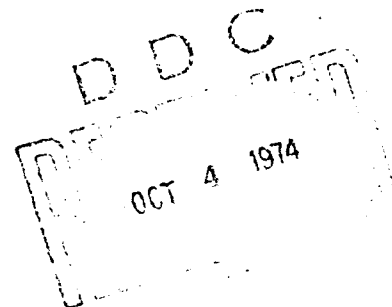Watertown, Massachusetts

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OCT 4 1974

EFFECT OF INTERLAYER ON IMPACT RESISTANCE OF ACRYLIC/POLYCARBONATE LAMINATES

JOYCE L. ILLINGER, Ms.
ROBERT W. LEWIS, ScD
DENNIS B. BARR, PhD
ARMY MATERIALS & MECHANICS RESEARCH CENTER
WATERTOWN, MA.

INTRODUCTION

Polymeric materials receive widespread application for lightweight transparent enclosures in aircraft and as spall protective devices for personnel. Currently, polymethylmethacrylate (PMMA) is the transparent polymeric impact-resistant material most frequently encountered in aircraft applications. PMMA, however, while much tougher and more impact resistant than glass, is relatively brittle and will spall upon ballistic impact, leading to possible injury to personnel behind the windshield (Figure 1). Rubber modification improves the impact resistance substantially, but causes the acrylic to lose transparency at low temperatures (1). Polycarbonate (PC) eliminates the spall problem (Figure 2) but has only slightly higher ballistic resistance than PMMA (V_{50} = 1100 ft/sec vs 1040 ft/sec for 17 grain Fragment Simulating Projectiles (FSP) at 38 oz/sq. ft.). In addition, PC has poor abrasion and poor solvent resistance.

A search for transparencies with improved ballistic protection coupled with non-spalling characteristics has led to the evaluation of the potential for plastic/plastic laminates (2). In the course of the evaluation it was found that PMMA/PC laminates markedly enhanced the ballistic resistance (Figure 3). At the extreme left in Figure 3 is the ballistic resistance of 100% PMMA with a V_{50} of 1040 ft/sec. At the extreme right is 100% PC with a V_{50} of 1100 ft/sec. With PMMA facing the impact (upper curve), the optimum ballistic resistance of the combinations tested occurred at a 2:1 weight ratio of PMMA to PC (V_{50} = 1400 ft/sec) in good

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agreement with the optimum ratios for glass to plastic (3). With the ductile PC facing the impact (the lower curve), however, there was a reduction in ballistic resistance compared to that of the homogeneous materials over the range of compositions investigated. The enhanced resistance of the clamped laminate was attributed (2) to the brittle PMMA spreading out the impact over a wider area than a ductile material, while the ductile PC serves both to absorb the impact and to prevent the brittle material from spalling. Thus, an improvement in ballistic resistance of about 27 percent was obtained over either material alone.

In order for a laminated system to be useful for aircraft applications, however, it is necessary to bond the materials together, either thermally or by the incorporation of an adhesive interlayer. Earlier work demonstrated, though, that both brittle adhesives (conventional polyvinylbutyral as well as transparent epoxies) and thermal bonds resulted in poor ballistic performance accompanied by spalling of the PC, caused by failure of the interlayer to cushion the impact loads transmitted from the facing PMMA. Consequently, it was found that a flexible interlayer is required to maintain the enhanced ballistic performance.

This paper describes an investigation of the relationships betweeen microstructure of transparent segmented polyurethane (PU) adhesives, their optical properties and laminate ballistic performance that has led to a forty-five percent advance in the state-of-the-art of ballistic resistance of transparent plastics.

EXPERIMENTAL

Synthesis and Composition

A standard two-step synthesis was used to prepare three series of adhesive polymers. The general structure may be represented as

$$M \sim\sim\sim [(MB)_x M \sim\sim\sim]_y M$$

where M (MDI) is $O=C=N-\bigcirc-CH_2-\bigcirc-N=C=0$;
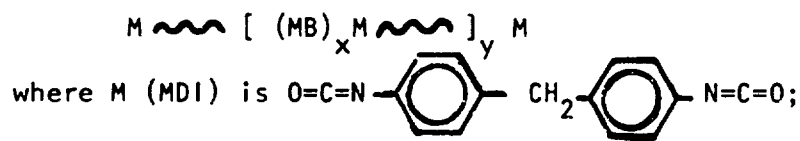
B (Bd) is 1, 4 butanediol, $HO\ CH_2CH_2CH_2CH_2OH$; and

$\sim\sim$ is a polymeric glycol, $HO(CH_2CH_2O)_a\ (CH_2\underset{\underset{CH_3}{|}}{CHO})_b\ (CH_2CH_2O)_aH$

Table I shows the variation in composition and structure of the available polymeric glycols.

All three series had y held constant. Series I was made using L35 as the glycol and varying x from 0 to 1.0 plus two additional polymers at x = 2.0 and 5.0. Series II was made holding x constant at 0.4 and making polymers using each of the seven polymeric glycols for the soft segment. Series III was similar to series II except that x = 0.5.

Sample Preparation for Electron Microscopy (Ultracryotomy)

Due to the nature of the polymers room temperature sectioning of samples for microscopy proved impossible. Hence cryogenic techniques had to be developed. The equipment used was an LKB Ultratome III with Cryo Kit attachment (LKB Instruments, Inc.) and Diamond Knife (DuPont). Small pieces were mounted in the sample holder on the microtome. The Diamond knife reservoir was filled with a mixture of DMSO and water (60/40). Sample temperatures were set between -70° and -167°C, although -100°C was generally the best temperature for all samples. The knife temperature was set at -50°C. Nominal section thickness was 1000Å. Sections wrinkled slightly as they were cut, but gentle heat supplied by resistance-heated platinum caused the sections to relax sufficiently. No morphological changes due to this heating were observed in the electron microscope. Sections were picked up on copper grids, washed in distilled water, and dried in a desiccator.

RESULTS AND DISCUSSION

Description and Characterization

The first series of polymers ranged from extremely sticky with very little elastomeric behavior to slightly tacky with very little permanent set (Table II). From x = 0.0 to x = 0.6 the polymers were transparent becoming transulucent at x = 0.8 and 1.0. The molecular weights of all but x = 0 are $\sim$ 40,000 so that the gradual change in tackiness, elastomeric properties, and transparency must be due to change in structure due to increasing butanediol content. Differential scanning calorimetry (DSC) was performed to determine T_g to see if there was any change with structure which might be related to ballistic performance. T_g shows a monotonic increase with increasing butanediol content (Figure 4) over a 15 C temperature range. Leveling off of T_g occurs above the butanediol content which remains transparent.

Table III summarizes the properties of series II and III.

It appears that increasing amounts of polypropylene glycol in soft segments of around 2000 molecular weight leads to trans- lucency at lower butanediol content.

T_g behavior of these series showed no meaningful change.

Microscopy

Figure 5 portrays optical micrographs of four of these materials showing changes in microstructure as a function of Butanediol ("hard segment") content. Figure 5a is a formulation with less than 1 mole of butane diol, and the polymer shows no structure. This material is transparent. Figure 5b shows a polymer which was translucent (1 mole Bd), and here isolated scattered spherulitic structure is apparent. At increased hard segment content more spherulites appear until finally (Figure 5d) at 5 moles hard segment the spherulitic structure is predominant. These latter materials are completely opaque.

Figure 6 shows transmission electron micrographs of the same polymers. At these much higher magnifications the lack of any structure in the transparent materials is obvious (Figure 6a). Structure in the isolated spherulites of the translucent materials is not highly regular but still enough to scatter light leading to loss of transparency. The very high hard segment composition material (Figure 6d) shows how highly intertwined these spherulitic structures have become. This accounts for the total opacity of the material. The dimensions of these spherulites are sufficiently large that they must include both soft and hard segments.

Ballistic Resistance of Laminates

Laminates from 1/4" PMMA, 10 mil adhesive, and 1/8" PC were fabricated at press conditions of 100 PSI at 95°C for 40 minutes residence time cooled under pressure. The results of ballistic evaluation are shown in tables IV and V.

As long as the adhesives used were transparent (no spherulitic structure present as seen by microscopy) the V_{50}'s of the laminates were essentially the same. The 1.0 butanediol content polymer was nontacky, indicating some embrittlement. The lowered ballistic performance is in agreement qualitatively with earlier observations on the effect of brittle adhesives.

As seen in Table V the structure of the polymeric glycol (molecular weight ∿ 2000) at constant MDI and butanediol composition had no significant effect on the ballistic performance of the laminates. These polymers were all transparent at the 10-mil thickness of the adhesive layer used for laminate evaluation.

The range of V_{50} from 1580 to 1600 ft/sec represents a forty-five percent improvement over either material alone (V_{50} = 1040 to 1100 ft/sec) and a 200 ft/sec increase over the laminate without interlayer. In addition, the laminate did not spall unlike the situation where a brittle adhesive was used (Figures 7 and 8). Thus, the transparent flexible PU adhesives satisfactorily meet the criteria for enhanced ballistic resistance while eliminating spallation.

Dynamic Mechanical Spectra

Structural changes occurring in polymeric materials are often characterized by examination of the dynamic mechnical properties as a function of temperature. Since these changes have been qualitatively related to impact and ballistic resistance (2,5,6), mechanical spectroscopy was included in our evaluation. Figure 9 shows dynamic mechanical spectra of several compositions of "hard segment in polymers made from L35. At lower Butanediol content there is a broad loss shoulder around -130°C which gradually sharpens into a peak with increasing hard segment composition. The glass transition temperature gradually moves to higher temperature with increasing hard segment content (also seen in the DSC measurements). Spectra for series III (1.576 MDI:0.5 Bd: 1 glycol) are essentially the same for all glycols used.

The composition at which the low temperature shoulder sharpens into a loss peak coincides with the first evidence of spherulitic structure, which also correlates with lowered ballistic resistance of laminates. Thus, the appearance of a low temperature loss peak is indicative of structural changes in the adhesive that is accompanied by reduced ballistic performance.

CONCLUSIONS

Acrylic/polycarbonate laminates for windshield applications fabricated using transparent flexible polyurethane adhesive interlayers have demonstrated ballistic resistance up to forty-five percent greater than polycarbonate, currently considered the best commercially available transparent impact-resistant material.

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Optical and transmission electron microscopy show that the translucent and opaque materials have spherulitic structures which are few in numbers at low "hard" segment concentration and densely packed at high concentration. Dynamic mechanical spectra revealed a glass transition temperature gradually increasing with hard segment content and a broad low temperature loss shoulder. As the hard segment content increases, the broad shoulder sharpens into a loss peak, coinciding with the formation of spherulitic structure accompanied by reduced ballistic performance.

So long as the materials showed no spherulitic structure, no real variation in ballistic performance was found with increasing "hard" segment. Variation in soft segment chemical composition also had no effect on the impact resistance. The mode of failure of these laminates was ductile contrary to thermally bonded laminates or laminates using a brittle adhesive, thereby eliminating the spallation problem inherent in the use of monolithic acrylic windshields. Thus, as long as spherulitic formation can be prevented, the ballistic resistance of polyurethane interlayered plastic laminates is superior to all other transparent plastic systems.

ACKNOWLEDGEMENT

The authors wish to thank Joseph M. Rogers for carrying out the ballistic tests, Richard W. Matton for preparing the polyurethane polymers and Robert Coulehan of CIBA-GEIGY Corp. for obtaining the dynamic mechnical spectra.

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Table I. GLYCOL COMPOSITION
AND STRUCTURE

Glycol	Composition	a	b
C1540	100% PEG	0	35
L35	50/50 PPG/PEG	11	17
L44	60/40 PPG/PEG	10	23
L43	70/30 PPG/PEG	6	23
L42	80/20 PPG/PEG	3	22
L61	90/10 PPG/PEG	2	33
P2010	100% PPG	34	0

Table II. VARIATION OF HARD SEGMENT

MDI	Bd	Glycol	Description	$\overline{M}_n \times 10^3$	Optical Properties
1.05	0	1	sticky, gradual flow, set	30,000	transparent
1.261	0.2	1	sticky, set, slightly elastomeric	39,000	transparent
1.471	0.4	1	tacky, less set, elastomeric	40,000	transparent
1.576	0.5	1	less tacky, still some set, elastomeric	40,000	transparent
1.681	0.6	1	slightly tacky, very little set, elastomer	41,000	transparent
1.891	0.8	1	little tack, very little set, elastomer	42,000	translucent
2.1	1.0	1	nontacky, no rapid set, elastomer	45,000	translucent
3.15	2.0	1	nontacky, elastomer	40,000	opaque
6.3	5.0	1	nontacky, elastomer	40,000	opaque

Table III. PROPERTIES OF SERIES II AND III

Glycol	Series II 1.471 MDI:0.4 Bd:1 glycol	Series III 1.576 MDI:0.5 Bd: 1 glycol
100% PEG	tacky, opaque in bulk (transparent in laminate)	tacky, opaque in bulk (transparent in laminate)
50/50 PPG/PEG	tacky, transparent	tacky, transparent
60/40 PPG/PEG	tacky transparent	tacky, translucent
70/30 PPG/PEG	sticky/tacky,transparent	tacky, transparent
80/20 PPG/PEG	sticky, transparent	sticky/tacky, transparent
90/10 PPG/PEG	sticky, translucent	sticky, translucent
100% PPG	very sticky, translucent	sticky, translucent

Table IV. EFFECT ON BUTANEDIOL CONTENT ON BALLISTIC PERFORMANCE

Polymer Series I Butanediol Content	V_{50} (ft/sec)	Optical Properties
0.0	1560	clear
.2	1570, 1600+	clear
.4	1510	clear
.5	1550, 1580+	clear
.6	1560	clear
1.0	1410	translucent

*17-grain FSP, 0° obliquity, PMMA facing, 8 shot V_{50}
+Determination of V_{50} for duplicate polymers

Table V.   EFFECT OF VARIATION OF POLYMERIC GLYCOL SERIES II AND III

V_{50} (ft/sec)*

Glycol	Series II 1.47 MDI:0.4 Bd: 1 glycol	Series III 1.576 MDI:0.5 Bd:1 glycol
100% PEG	1580	1584
50/50 PPG/PEG	1510	1550, 1580+
60/40 PPG/PEG	----	1585
70/30 PPG/PEG	1586	1584
80/20 PPG/PEG	1626	1581
90/10 PPG/PEG	1592	1602
100% PPG	---	1580

* 17-grain FSP, 0° obliquity, PMMA facing
+ Determination of V_{50} for duplicate polymers

Fig. 1.   Multiflash photograph of 1/4" PMMA under ballistic
          impact with 17 grain FSP, 0° obliquity. Edge of
          sample is shown, missile is moving from left to
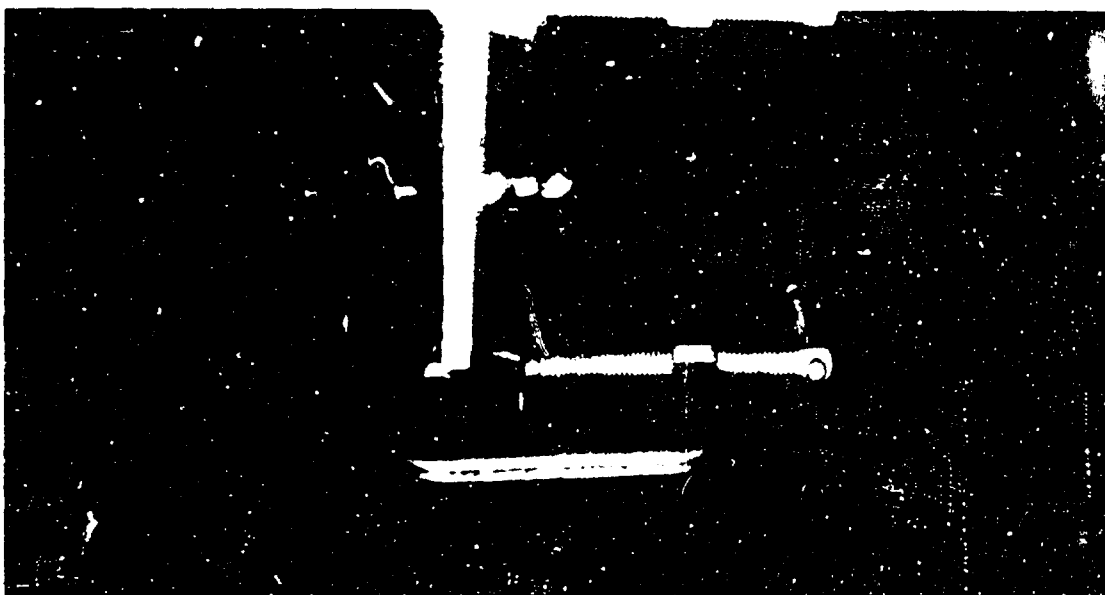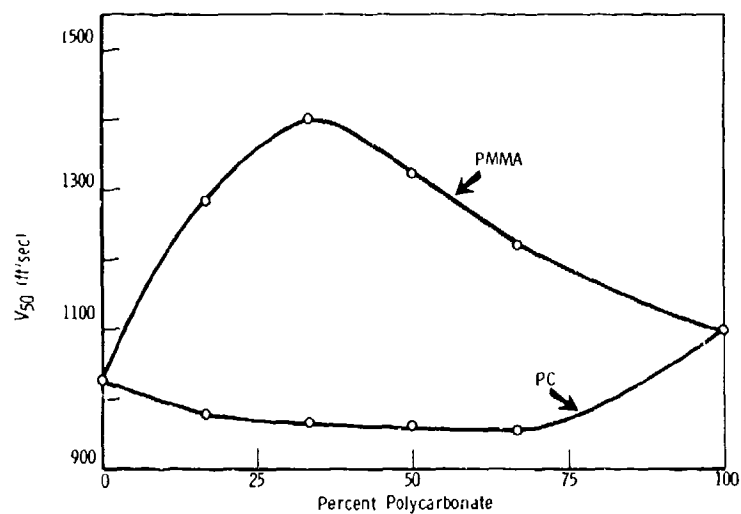   right.   Projectile was completely stopped by sample.

Fig. 2.   Multiflash photograph of 1/4" PC under ballistic impact
          with 17 grain FSP, 0° obliquity. Edge of sample is
          shown, missile is moving from left to right.   Note
          absence of spall.

Fig. 3.   Ballistic behavior of PMMA/PC laminates without
          interlayer.   (17-grain FSP, 0° obliquity, 38 oz/sq.ft.)
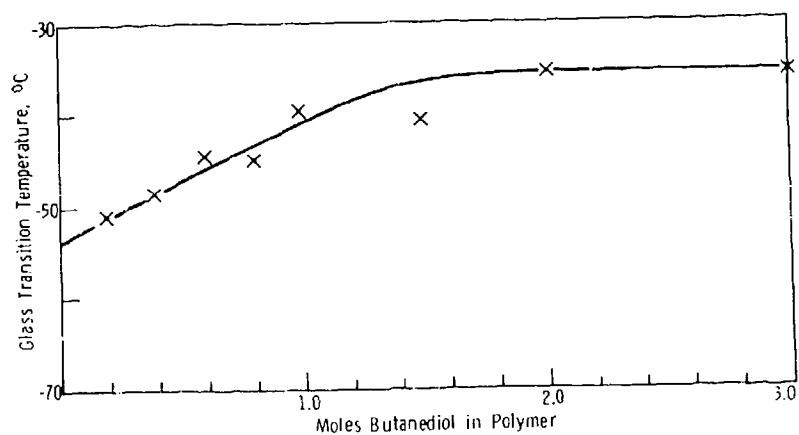
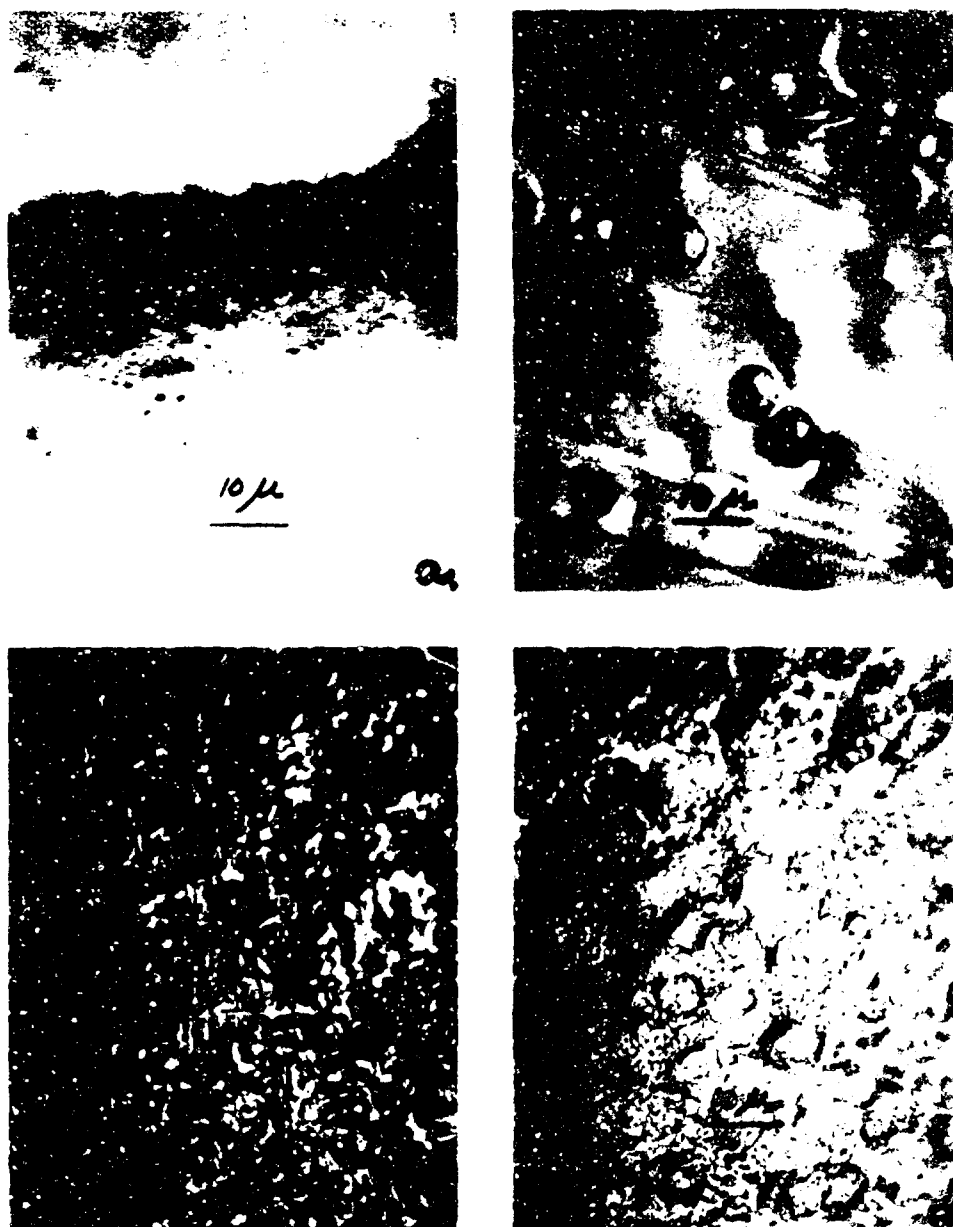Fig. 4.   Glass transition temperature versus butanediol content

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Fig. 5. Optical micrographs showing development of spherulitic
structure
a. 1.57 MDI 0.5 Bd: 1.0 Polyol
b. 2.10 MDI: 1.0 Bd: 1.0 Polyol
c. 3.15 MDI: 2.0 Bd: 1.0 Polyol
d. 6.30 MDI: 5.0 Bd: 1.0 Polyol

Fig. 6. Transmission electron micrographs showing details of spherulitic structure
   a. 1.57 MDI: 0.5 Bd: 1.0 Polyol
   b. 2.10 MDI: 1.0 Bd: 1.0 Polyol
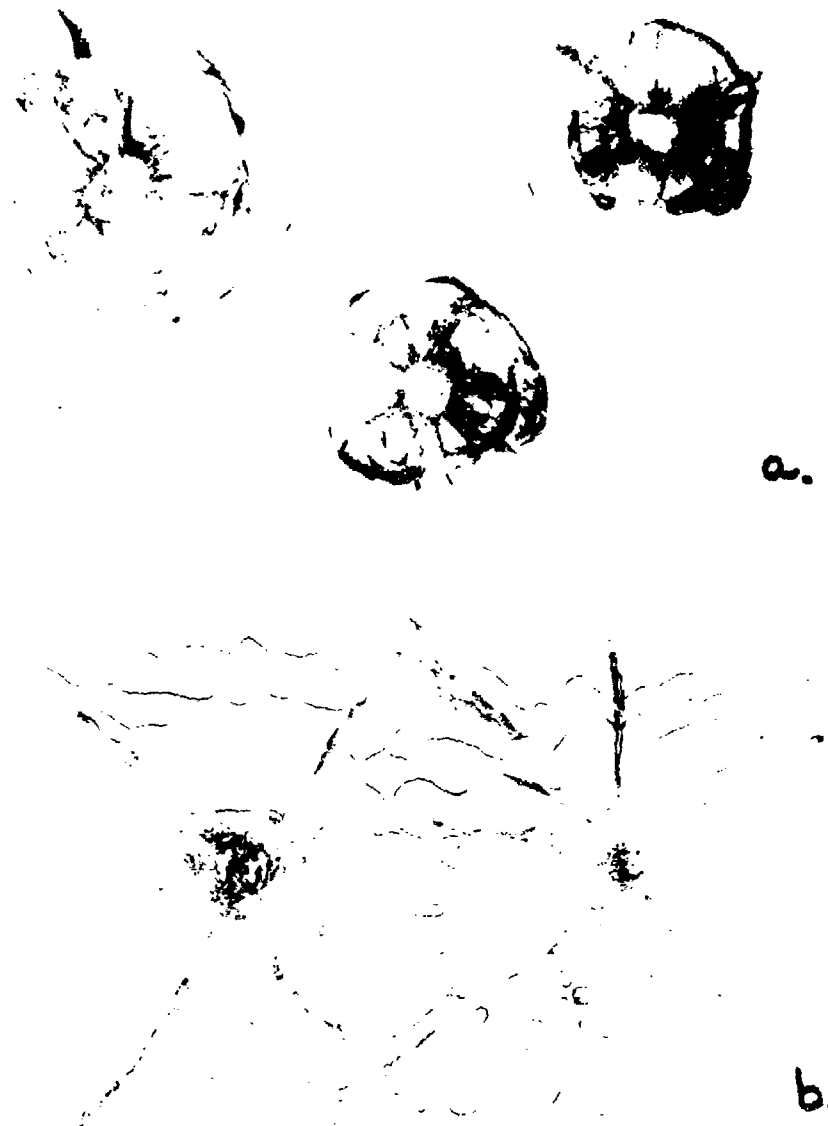   c. 3.15 MDI: 2.0 Bd: 1.0 Polyol
   d. 6.30 MDI: 5.0 Bd: 1.0 Polyol

Fig. 7. Comparison of brittle failure of PMMA/PC laminate
with ductile failure when flexible adhesive
layer is incorporated.
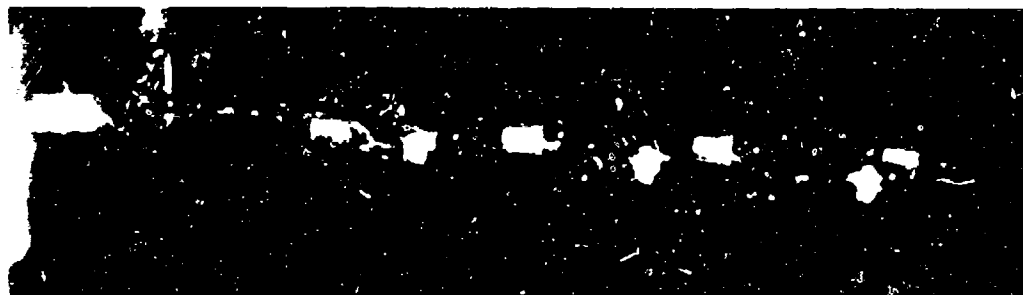a. Thermally Bonded PMMA/PC
b. PMMA/PU/PC

Fig. 8.   Multiflash photograph of 1/4" PMMA/Pu Adhesive/1/8" PC under ballistic impact with 17 grain FSP, 0° obliquity. Note absence of spallation.
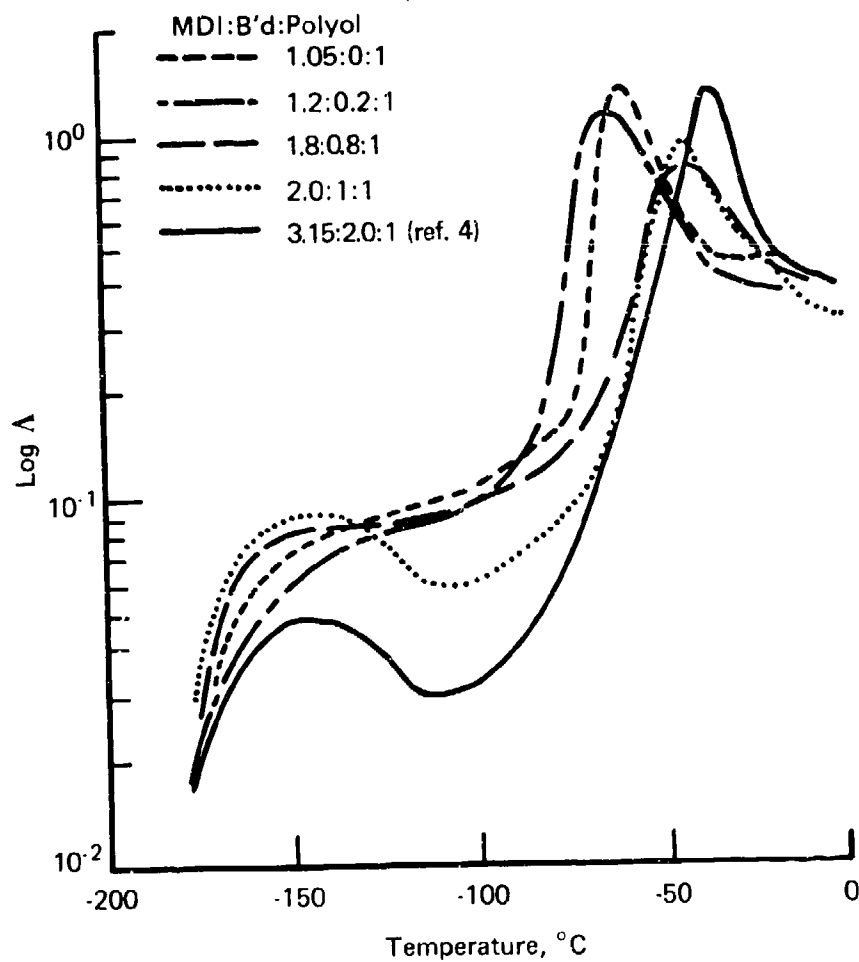

Fig. 9.   Dynamic mechanical spectra of PU adhesives.